



TITLE:

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CITATION:

Muranaka, Shigetoshi ...[et al]. Growth and Electrical Properties of FeMeX (Me=Ti, V; X=S, Se) Single Crystals. Bulletin of the Institute for Chemical Research, Kyoto University 1974, 51(5): 287-294

ISSUE DATE:

1974-01-28

URL:

<http://hdl.handle.net/2433/76503>

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Growth and Electrical Properties of FeMe_2X_4 ($\text{Me}=\text{Ti}, \text{V}$; $\text{X}=\text{S}, \text{Se}$) Single Crystals

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Received September 22, 1973

Single crystals of FeMe_2X_4 ($\text{Me}=\text{Ti}, \text{V}$; $\text{X}=\text{S}, \text{Se}$) were grown by the isothermal vapor growth in the closed tube, using Cl_2 or TeCl_4 as a growth agency. The sizes of crystals produced were $3 \times 2 \times 0.8 \text{ mm} \sim 10 \times 1 \times 0.8 \text{ mm}$. The temperature dependence of electrical resistivity from 78°K to 350°K and the thermoelectric power at room temperature were measured on single crystals. These measurements showed that FeMe_2X_4 exhibited metallic behaviors.

INTRODUCTION

In recent years the preparation and structural properties of ternary chalcogenides having the formula FeMe_2X_4 ($\text{Me}=\text{Ti}, \text{V}$; $\text{X}=\text{S}, \text{Se}$) were reported.^{1,2,3} All were found to have the monoclinic defect NiAs structure (space group 12/m) which was first proposed by Jellinek for Cr_3S_4 .⁴ In this structure cation vacancies are confined to alternate metal layers; anions are in hexagonal array. The magnetic properties of FeMe_2X_4 have been reported by Plovnick *et al.*⁵ and one of authors.⁶ They are antiferromagnets with the Néel temperature of 94.5–138°K. The electrical properties of FeTi_2S_4 and FeTi_2Se_4 were studied by Plovnick *et al.*, using polycrystalline samples.⁷ They were found to exhibit metallic behaviors, as indicated by their low resistivity and small thermoelectric powder. It is of interest to investigate precisely the magnetic and electrical properties of FeMe_2X_4 , using the single crystal samples. In addition to the interests of the magnetic and electrical properties, the phenomenon of structural change, for example order—disorder transition of vacancies, is attractive from the point of view of understanding the stability of vacancies which are included in FeMe_2X_4 . Therefore, it was desirable to use the single crystals for these sample.

The single crystals of FeMe_2X_4 were grown by the isothermal vapor growth in the evacuated silica tube, using Cl_2 or TeCl_4 as a growth agency. In this paper the method on single crystal preparation is reported together with the results of the electrical resistivity and thermoelectric power measurements.

The magnetic and structural studies of FeTi_2X_4 have been partly reported elsewhere, using the single crystals obtained in this growth experiment.^{8,9}

EXPERIMENTALS

1. Growth Procedure

The sealed tube for the vapor growth reaction was prepared by the following way.

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Powder sample of FeMe_2X_4 of about 1 g was loaded in the transparent silica tube of 13 mm in diameter and 70 mm in length. After the tube was evacuated to 10^{-6} mmHg, Cl_2 gas was introduced into the tube as a growth agency and then the tube was sealed off. In the case of TeCl_4 , which was treated in the dry box, it was put in before evacuating the tube. The sealed tube was kept for one week in the horizontal furnace, where the temperature was kept constant within $\pm 2^\circ\text{C}$. The products consisted of many crystals up to 10 mm in length and up to 2 mm in width. Chlorine atoms enclosed in the grown crystals were eliminated by the heat treatment at $900\sim 1000^\circ\text{C}$ in the sulfur or selenium atmosphere.

Chemical analyses were carried out for the obtained crystals, the residual powder samples and the starting samples. The crystals of 5~15 pieces, total amount of which had the weight of 100~200 mg, was crashed and powdered. The amount of sulfur was calculated from the weight change upon complete oxidation of the sample, based on the amount of metal atoms. The metal atoms were analysed magnetically. The oxidized products of FeTi_2S_4 and FeTi_2Se_4 were composed of Fe_2TiO_5 and TiO_2 ; while those of FeV_2S_4 and FeV_2Se_4 were of FeVO_4 and V_2O_5 . It was found that the magnetic susceptibility of the mixture of Fe_2TiO_5 and TiO_2 (or FeVO_4 and V_2O_5) changed linearly with the ratio of iron to titanium or vanadium atoms in the range of $\text{Fe}/(\text{Fe}+\text{Ti})$ (or $\text{V})=0.3\sim 0.37$. In advance the curves of the susceptibility versus the metal ratio were made using the standard samples. These curves were shown in Fig. 1. In this procedure the metal ratios were determined within the accuracy of 0.02 atomic %. Besides these magnetic analyses, the metal ratios of starting samples were also analysed by the usual precipitation method after dissolution of the oxidized product into the acidic solution. Both results were in good agreement.

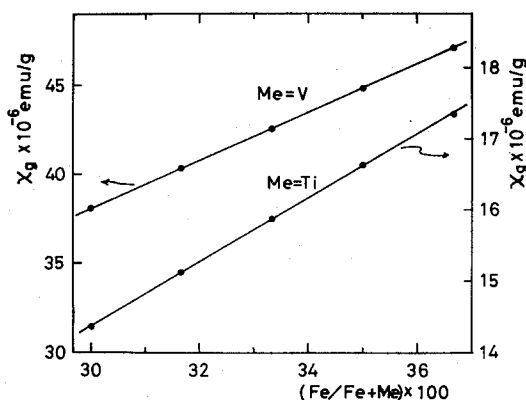


Fig. 1. Standard curves of the susceptibility versus the metal ratio.

2. Phase Identifications and Measurements

The crystals obtained were confirmed to be single crystals by the X-ray precession method. The lattice parameters were determined by the X-ray diffraction method. Néel temperature was determined from the peak of the magnetic susceptibility, using the torsion balance magnetometer.

The measurements of electrical resistivity were carried out along the growth axis of crystals by means of four point method, using a d. c. potentiometer. The thermo-

electric powers were measured by the copper wires and Cu-AuCo thermocouple which were attached to both ends of a crystal using silver paste. The temperature difference between both ends of a crystal was kept to be $2\sim 4^\circ\text{C}$. The values found were corrected for the thermal e. m. f. of the copper wires used as leads to the samples. This correction was taken to be $+3.1 \mu\text{V/K}$ at room temperature.

RESULTS AND DISCUSSION

1. Crystal Growth

Many crystal growth experiments of sulfides and selenides have been based on the vapor transport method in the closed tube, because of the difficulties of the vapor pressure control and the unstable behaviors at temperatures well below their melting points.

Crystal growth experiments of FeMe_2X_4 ($\text{Me}=\text{Ti}, \text{V}$; $\text{X}=\text{S}, \text{Se}$) by the chemical transport method were tried under various heat gradients, using Cl_2 , I_2 or TeCl_4 as a transport agent. When the pressure of the transport agent was over 0.8 atm at room temperature, FeTi_2S_4 was transported from the high temperature source zone to the low temperature crystalizing zone with the temperature difference of 100°C , depending on the kind of carrier gas. On the other hand, when the pressure of carrier gas was below 0.3 atm, FeTi_2S_4 was scarcely transported under any heat gradients, but crystalized at the starting hot zone. The crystals obtained at the starting zone in the latter procedure were a few times larger than those transported in the former procedure. Similar tendency was observed for the growth of FeV_2S_4 , FeTi_2Se_4 and FeV_2Se_4 .

Since our purpose is to obtain the perfect, large single crystals, crystals were grown in the short tube under no temperature gradient, using Cl_2 , I_2 or TeCl_4 as a growth agency. Without the introduced halogen gas, the crystals were not grown at any temperatures. Therefore, the crystal growth in this isothermal system seems to progress by forming more volatile chemical intermediates such as FeCl_2 and TiCl_3 (or VCl_3). In this sense our isothermal crystal growth is one of the chemical transport reaction. The vaporization and deposition of starting substances presumably take place successively by forming the volatile intermediates of halogenides between somewhat different temperatures.

The optimal conditions of vapor growth reaction for FeMe_2X_4 are listed in table I, together with sizes and colours of the crystals obtained. Chlorine was the most suitable gas for the growth of FeTi_2S_4 , FeTi_2Se_4 and FeV_2Se_4 , while TeCl_4 was for that of FeV_2S_4 . The obtained crystals of FeTi_2S_4 were often triply twinned. This tendency was increased with an increase of temperature and of the pressure of Cl_2 .

Table I. Optimal Growth Conditions and Properties

	Temperature	Growth agent	color	size
FeTi_2S_4	900°C	70 mmHg (Cl_2)	metallic black	$6 \times 2 \times 0.2 \text{ mm}^3$
FeV_2S_4	900°C	0.6 mg/cm^3 (TeCl_4)	metallic grey	$10 \times 1 \times 0.8 \text{ mm}^3$
FeTi_2Se_4	1000°C	40 mmHg (Cl_2)	metallic black	$4 \times 2 \times 0.6 \text{ mm}^3$
FeV_2Se_4	1000°C	30 mmHg (Cl_2)	metallic grey	$3 \times 2 \times 0.8 \text{ mm}^3$

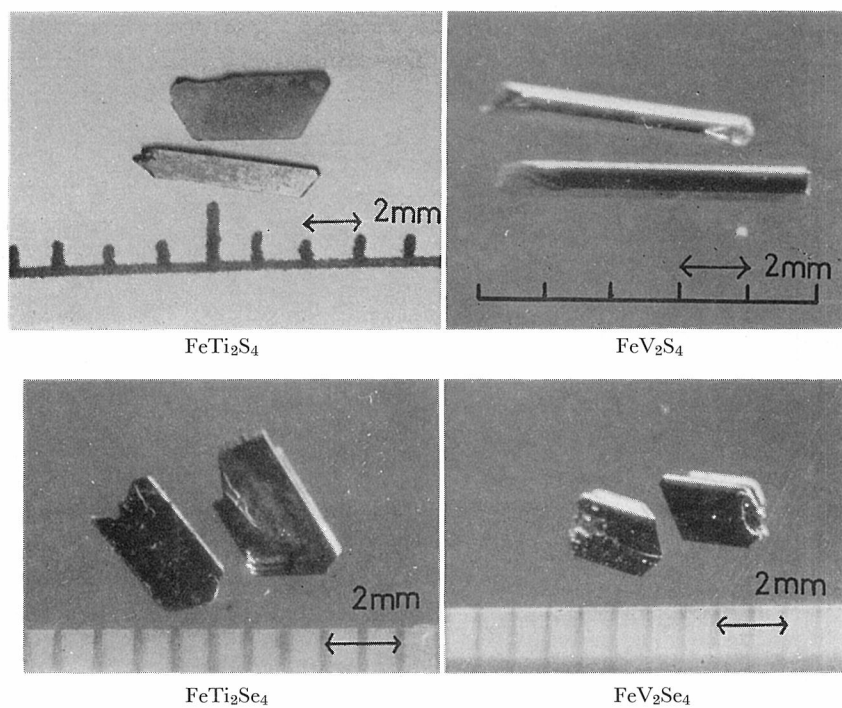


Fig. 2. The photographs of single crystals of FeTi_2S_4 , FeV_2S_4 , FeTi_2Se_4 and FeV_2Se_4 .

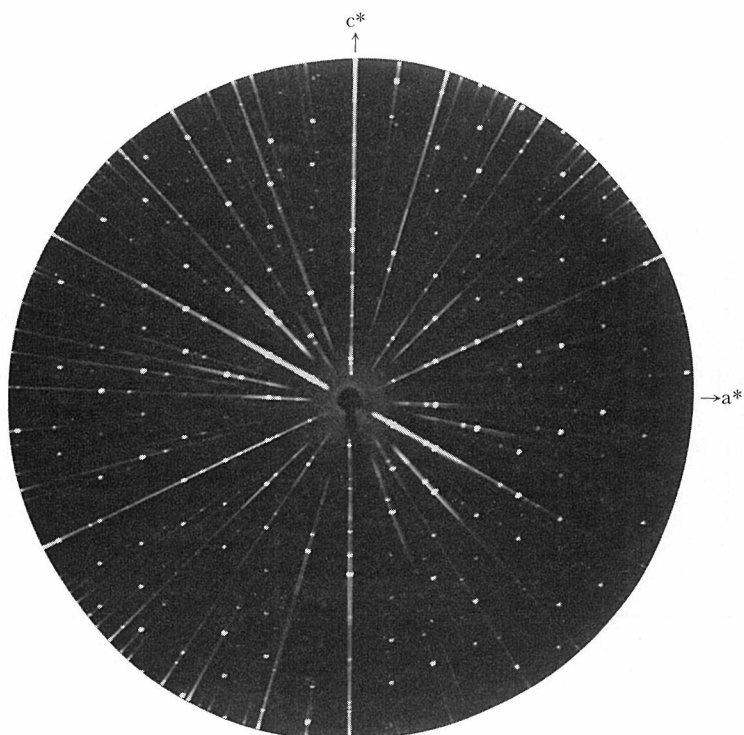


Fig. 3. The precession photograph of FeV_2S_4 . The c^* and a^* axes are vertical and horizontal directions, respectively.

The crystal growth of FeV_2S_4 , FeTi_2Se_4 and FeV_2Se_4 showed similar tendency.

Figure 2 shows the photographs of single crystals obtained. The crystals have a tendency to grow in the direction of the crystallographic b-axis. The best developed plane was (002) and the next (101).

From the X-ray precession photographs, it was confirmed that the obtained crystals of FeMe_2X_4 were single crystals. The precession photograph of FeV_2S_4 is shown as a representative one in Fig. 3. The c^* and a^* axes are vertical and horizontal directions, respectively.

The lattice parameters of the crystals are listed in table II, together with those of

Table II. Lattice Parameters of FeMe_2X_4 Single Crystals and the Starting Substances.
The Values in Parentheses are from the References (1), (2) and (3).

	a (Å)	b (Å)	c (Å)	B (Å)
FeTi_2S_4 crystal	5.926	3.428	11.457	90.1
starting	5.927 (5.929)	3.428 (3.426)	11.458 (11.46)	90.1 (90.10)
FeV_2S_4 crystal	5.868	3.297	11.298	92.05
starting	5.869 (5.87)	3.297 (3.30)	11.299 (11.33)	92.00 (91.95)
FeTiSe_4 crystal	6.223	3.587	11.952	90.23
starting	6.225 (6.221)	3.587 (3.582)	11.962 (11.93)	90.20 (90.25)
FeV_2Se_4 crystal	6.189	3.472	11.780	91.62
starting	6.186 (6.16)	3.472 (3.47)	11.787 (11.80)	91.58 (91.60)

Table III. Chemical Analysis Data of FeMe_2X_4 Crystals, Starting Substances and Residual Ones.

	Fe atomic %	Ti atomic %	S or Se atomic %
calculated	14.29	28.57	57.14
FeTi_2S_4 crystal	14.37	28.52	57.12
starting	14.25	28.64	57.11
residual	14.23	28.67	57.10
FeV_2S_4 crystal	14.48	28.35	57.17
starting	14.23	28.59	57.13
residual	14.11	28.73	57.17
FeTi_2Se_4 crystal	14.23	28.50	57.27
starting	13.80	29.00	57.20
residual	13.41	29.44	57.14
FeV_2Se_4 crystal	14.72	27.95	57.33
starting	14.16	28.58	57.27
residual	13.63	29.19	57.17

the starting substances and those from references 1, 2 and 3. They were for the most part in good agreement within the experimental errors ($\pm 0.005 \text{ \AA}$).

Table III shows the results of chemical analyses. It was found that there were always the slight difference in the composition between the crystals obtained and the starting substances. Compared with the respective starting substances, the crystals were rich in Fe atoms by 0.1~0.3 atomic % for FeTi_2S_4 and FeV_2S_4 , while they were by 0.4~0.6 atomic % for FeTi_2Se_4 and FeV_2Se_4 . On the other hand, the residual substances at source zone after the growth experiment were rich in Ti or V atoms.

The contaminations of Cl and Te in the grown crystals were detected spectroscopically. Chlorine was fairly contained in the crystals. The crystals of FeTi_2S_4 and FeV_2S_4 contained chlorine much more than those of FeTi_2Se_4 and FeV_2Se_4 . In order to remove chlorine from the crystals, the crystals were heated at $900^\circ\text{C}\sim 1000^\circ\text{C}$ in evacuated silica tube and in the atmosphere of sulfur or selenium vapor. Chlorine was scarcely eliminated by the former procedure, but considerably eliminated by the latter procedure. It is, therefore, considered that the chlorine atoms occupied the positions of sulfur or selenium atoms in the lattice. Since the ionic radius of chlorine is closer to that of sulfur than selenium, sulfur seems to be more easily replaced by chlorine than selenium in the growing process of the crystals. Table IV shows the contamination of Cl and Te in the grown crystals before and after the heat treatment in sulfur or selenium atmosphere.

Table V shows the Néel temperature of various specimens. The Néel temperatures of the FeMe_2X_4 crystals obtained were slightly different from those of the respective starting substances. This may be mainly attributed to the difference of the chemical composition. The Néel point changed also with the condition of heat treatment during the sample preparation. The Néel points of FeV_2S_4 , FeTi_2Se_4 and FeV_2Se_4 , when quenched from 900°C , were 114 K, 129 K and 89 K, respectively. The Néel

Table IV. Spectrographic Analyses of Cl and Te (weight %). (The values in parentheses are those after the heat treatment in sulfur or selenium atmosphere.)

	Cl	Te
FeTi_2S_4	0.1~0.3% (0.02%)	
FeV_2S_4	0.08% (0.02%)	0.015% (0.008%)
FeTi_2Se_4	0.07% (0.009%)	
FeV_2Se_4	0.04% (0.008%)	

Table V. Néel Temperatures (K) of Single Crystals, Starting Materials and the Results of Plovnick *et al.*

	Single crystals	Starting materials		Plovnick <i>et al.</i>
		slow cooling	quenching	
FeTi_2S_4	138	138	—	—
FeV_2S_4	138	140	114	131
FeTi_2Se_4	133	136	129	134
FeV_2Se_4	100	107	89	94.5

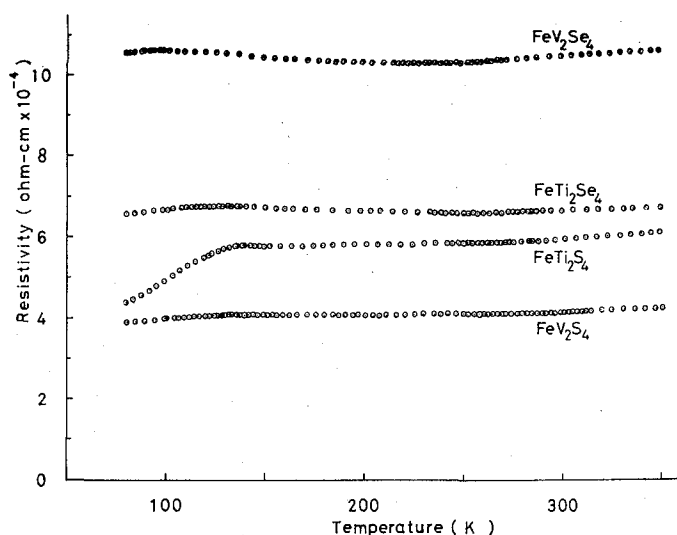


Fig. 4. The temperature dependence of electrical resistivity of FeTi_2S_4 , FeV_2S_4 , FeTi_2Se_4 and FeV_2Se_4 .

point of FeTi_2S_4 was greatly affected by the heat treatments of specimen as already reported.⁶⁾ On account of these two factors, the Néel temperatures of crystals seem to be different from those of the starting materials. The differences between Néel point of the starting materials and those obtained by Plovnick *et al.* were also attributed to these causes.

2. Electrical Properties

The electrical resistivity of FeMe_2X_4 was measured from 78 K to 360 K. As shown in the curve of Fig. 4, a change in slope was found at the Néel temperature of FeTiS_4 , FeTi_2S_4 , FeTi_2Se_4 and FeV_2Se_4 , respectively. Therefore, a change in slope can be attributed to the magnetic transitions from antiferromagnet to paramagnet of FeMe_2X_4 .

The resistivity of FeTi_2Se_4 measured on single crystal sample was similar to the result obtained by Plovnick *et al.* However, the distinct change in slope at Néel temperature of FeTi_2S_4 was not observed in their result. This is due to the difference of heat treatments in the sample preparations.

The thermoelectric powers of FeMe_2X_4 were measured at room temperature. The thermoelectric powers of FeTi_2S_4 , FeV_2S_4 , FeTi_2Se_4 and FeV_2Se_4 were -1.9 , $+3.0$, -6.8 and -2.0 $\mu\text{V/K}$, respectively. The values of FeTi_2S_4 and FeTi_2Se_4 obtained by Plovnick *et al.* were $-4 \sim -14$ $\mu\text{V/K}$.

Plovnick *et al.* explained the metallic behaviors of FeTi_2S_4 and FeTi_2Se_4 as indicated by the low resistivity ($10^{-3} \sim 10^{-4}$ Ωcm) and the small thermoelectric power ($-4 \sim -14$ $\mu\text{V/K}$) on the bases of critical distance model proposed by Goodenough.¹⁰⁾ According to this model, the critical distance for the direct overlap, R_c , between Ti^{3+} atoms is estimated to be 3.52 Å for sulfide and 3.62 Å for selenide. The separation of Ti-Ti along the b-axis in FeTi_2S_4 and FeTi_2Se_4 are 3.4 Å and 3.6 Å, respectively. Therefore, they concluded that the 3d-electrons of Ti atoms in these crystals are not localized and contributed to their metallic conductivity.

The metallic conductivity of FeV_2S_4 and FeV_2Se_4 was explained by the same model. The critical distance for V^{3+} ions in sulfide and selenide are estimated to be 3.42 Å and 3.52 Å, respectively. The separations of vanadium atoms in the direction of the b-axis in FeV_2S_4 and FeV_2Se_4 were 3.3 Å and 3.5 Å, respectively. Therefore, it is considered that the electrons of vanadium atoms are not localized by the direct overlap of V^{3+} .

ACKNOWLEDGMENTS

The authors are indebted to Prof. Yoshichika Bando and Dr. Shinjo for helpful discussions and Mr. Masao Kiyama for his guidance and continuous encouragement. Thanks are also due to Dr. Shigeo Nakajima for his help of X-ray precession experiments.

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